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Item #5a

Experience gained from the operation of Alkazid-desulphurization plants

The recommendations which are compiled in the following article do not refer specifically to the alkacid process, but should always be observed if plants of such kind must be operated.

A. Transport and storage of Alkazid-lyes

The liquid is completely harmless and not dangerous to handle. It is not cauterizing, not inflammable, and normally non-poisonous. However it is advisable not to bring in contact with the skin over a long period of time. Hands should be washed carefully after handling the liquid. It is possible that a fresh liquor containing small amounts of poisonous substances which, however, are quickly vaporized during the operation of the plant.

The liberated gases may contain poisonous substances. It is recommended, therefore, during storage in closed containers:

1. to avoid extremely high temperatures
2. to lift the stoppers of the containers from time to time.

If solid salt crystals should have been deposited, they can be easily dissolved by heating the liquid by means of steam. It is also possible to separate the salt deposits from the liquid and to dissolve them by means of water. The solution is united with the original liquid. The storage containers should not be filled up completely.

Only steam condensate should be employed for the dilution of the liquid. It is of advantage to cool drums, which contain alkazid solution and inside of which a certain pressure can be expected due to a preceding heating, by means of a water spray. The reduced gas pressure eliminated the possibility that the escaping gases will carry away parts of the liquid. Alkazid solutions which have been stored over a long period of time should be investigated with reference to their corrosivity against aluminum.

A. Slight corrosivity can be eliminated by the addition of water glass.

3. Start of an Alkazid plant

1. All parts of the plant must be completely tight before starting the operation.

Leaking pipes and apparatus may cause considerable losses of money by losing the valuable liquor. Due to the high poisoning effect of hydrogen sulfide, the pipes must be completely gas tight if hydrogen sulfide is to be extracted from the gas. In order to be able to recognize leaking pipe connections of the apparatus it is advisable to operate the plant with water over a short period of time with the recirculation of large volumes of water. The water should be changed for several times in order to remove all rust and dirt from the apparatus. The distributing trays of the washer and column must be adjusted very carefully. (Only a uniformly distributed liquid secures a high extracting efficiency.)

Should parts of the plant consist of aluminum, water glass (1 liter per cu. m. of water) should be added to the recirculating water because the resistance against corrosion of the aluminum can be greatly improved by this treatment. Only a cold liquid, the temperature of which should by no means exceed 60°F., should be recirculated. Only such water must be employed which has no corroding properties against aluminum. Steam condensate is the most suitable water for that purpose. Should additional aluminum parts be installed to the plant they must be treated with a 10% water glass solution before installation.

2. ~~Fresh or refreshed alkazid solution can be charged into the~~ apparatus provided all water is drawn off and the purging column of heat exchanger is cold. It is advisable to pump a highly concentrated alkazid solution into the apparatus because it will be diluted by the ever present water. The liquid is recirculated over such a period of time until the air is completely removed from the liquid carrying pipes which are provided with suitable vents to allow the air to escape.

Such a volume of liquids should be introduced so that its level in the purging column is of a hand's breadth higher than the exit of the pipe system of the boiler. The washer jump or the washer receiver should be half filled.

With the circulation shut down higher levels of the liquid will be observed because the surface of the "Raschig rings" of the wash tower and the purging apparatus retain certain volumes of the liquid. The volumes vary with the operating conditions and were determined with 35-75 liters per cu. m. of "Raschig rings" if the size of the rings is 25 x 25 mm.

3. If gas must be purged from the apparatus it should be born in mind that a refreshed lye will easily absorb CO_2 and that a cold solution which is saturated with CO_2 will occasionally deposit solid salts. If no gas free or almost free from CO_2 should be available, the oxygen should be replaced from the scrubber by CO_2 -gas whereafter the CO_2 is purged by means of a fuel gas before the alkazid solution is introduced. The air can be purged by steam from the column.

4. If the purification apparatus still contains CO_2 or H_2S from the previous operation, the introduction of CO_2 can take place only after heating the apparatus. Should a refreshed solution be pumped into the column it would absorb CO_2 and H_2S very easily causing reduced pressure inside the gas outlet pipes whereby the sheets of small gasholders can be destroyed.

5. As soon as the purification apparatus has the proper temperature (100°C . in the sump) the purification and recirculation of the liquid should not be continued over a long period of time, because an alkazid solution, which is stripped of CO_2 and H_2S to a high degree possesses slightly corrosive properties.

C. Operating conditions

1. The most favorable temperatures measured in the refreshed solution before its entrance into the scrubber are as follows:

for H_2S -extraction --- $20-25^\circ\text{C}$.

for CO_2 -extraction --- $25-55^\circ\text{C}$.

Alkzid solutions of high specific gravity should not be cooled to lower temperatures over a long period of time. Especially below temperatures of 20°C ., they have the tendency to form salt deposits.

2. The purification rate depends on the actual circumstances and must be determined for each single plant.

3. The steam which must be introduced into the boiler is subdivided into live steam and indirect steam in order to maintain the proper concentration of the liquid. If the gas to be extracted carries water, it is often necessary to reduce the volume of the introduced live steam and to increase the volume of the indirect steam. The same must

be done, if due to the small size of the purging apparatus (high heat losses) condensations of the steam takes place in its upper sections.

Considering larger plants approximately 50 kg. of indirect steam are consumed; the volume of introduced live steam, depending on the total steam consumption, is between 30 and 250 kg. per cu. m. of alkazid solution. By the distribution of the live and indirect steam or by the control of the reflux of the condensate, a uniform specific gravity of the refreshed alkazid solution is maintained. The specific gravity of the solution is determined by means of a hydrometer. Saturated solutions which have a spec. gravity higher than 1.20 show the tendency to form deposits at low temperatures which, however, can be dissolved by dilution or heating the solution. Hot solutions of a spec. gravity lower than 1.16 will occasionally corrode the aluminum parts of the plant. The steam which is used for the direct heating of the plant must be dry and free from impurities, such as NaCl , Na_2SO_4 . If the boiler is made out of aluminum, the steam must be completely free from caustic alkalis.

4. Output of the purification apparatus

Overloading of purification apparatus should be avoided in order to prevent a "carrying over" of the liquid which causes losses of the valuable alkazid solution. Fresh solutions sometimes have the tendency to foam for a short period of time. If it is not possible to reduce substantially the foaming by reducing the output, small amounts of an anti-foaming agent (Anti-foam I Leuna, 1-2 liter per 10 cu. m. of alkazid solution) should be added. The foaming of the solutions ceases mostly after 1 day of operation.

5. It is advisable to take continuous readings of the temperature and the pressure as shown by the attached forms of the Leuna alkazid-sulfur-extraction plant.

6. From time to time to time the solution should be investigated as shown by the attached form:

- a) Rate of gas absorption of the solution
- b) Efficiency of the purification apparatus
- c) Stability of the solution

It is of advantage to store away 1 sample of the liquid per month, in order to carry out special investigations.

7. If some parts of the plant consist of aluminum, corrosion tests should be performed at intervals of a few days. With the first signs of a beginning of aluminum corrosion water glass must be added to the solution. The maximum quantity of water glass which is added should not exceed a batch of 300 g. sodium silicate per cu. m. of solution (calculated on solid, water free salt). Should higher quantities be necessary they must be added in portions. It is of advantage to use the commercial solution (36-38°Be'; spec. grav. 1.33-1.35, $\text{Na}_2\text{O}:\text{SiO}_2 = 1:3.2-3.5$. The solution contains 34.4% Na_2SiO_3). It is diluted with 10 volumes of water before addition. As soon as the water glass solution is added, the liquid must be carefully mixed and recirculated. If the water glass is added to the recirculating liquid, it must be added continuously over a time during which the total charge is once recirculated.

By the water glass treatment, the alkazid solution is brought back to the non-corrosive state. Should substantial deposits be formed after boiling, they must be separated by filtration. The formation of deposits can be easily observed by boiling the alkazid solution in a beaker. In addition the specific gravity of the solution should be checked.

If even after a repeated treatment of the solution with water-glass and with the proper specific gravity of 1.16 the solution is still corrosive, a local dilution of the liquid during its passage through the purging apparatus can be expected. Local dilutions of the liquid occur if an improper introduction of the live steam into the column or if an unsuitable returning of the condensate takes place.

8. If H_2S or CO_2 containing H_2S is extracted, it must be kept in mind that especially the warm fouled liquid reacts with oxygen and forms thiosulfates. Since thiosulfate cannot be refreshed, the absorptivity of the solution will be proportionally reduced.

It was often observed that high speed pumps showed reduced pressure in the suction line and that they sucked in air through the stuffing boxes whereby a deterioration of the liquid took place.

At the Leuna-Alkazid plant, solution leaking from the pumps due to leakage is collected in a small container which is kept under nitrogen pressure. Nitrogen can be replaced by another type of oxygen-free gas such as water gas.

9. Alkazid solutions which have been selected for a special purpose, should not be employed for another kind of extraction because different alkazid solutions have different properties and in addition are susceptible to various substances which are present in the gas.

As soon as the absorptiveness of the solution deteriorates, it must be investigated whether it is due to the influence of oxygen hitherto not known or other constituents of the gas.

10. If despite satisfactory properties of the solution, the latter is showing an insufficient absorptiveness, improper distribution of the solution in the scrubbers may be expected. It must be checked whether the distributing tray is properly operating and whether the scrubber is satisfactorily filled with the solution.

11. Catch pots are inserted into the lines in order to protect the pumps from solid material which is carried in the recirculating liquid. The catch pots must be cleaned from time to time in order to secure a free passage for the solution. This is especially necessary for the catch pot which is situated before the hot pumps. The hot pump is operated with a liquid at a temperature which is near the boiling point. As soon as the vacuum increases inside the pump due to an insufficient supply, the liquid will begin to boil. By the formation and breaking-up of the steam bubbles the metal of the pumps will be strongly attacked. It is therefore very important that the feed-pressure of the pumps is not reduced by a choked catch pot.

12. Mercury must be very carefully kept away from the plant and the liquid if aluminum is employed for the design of the plant. Sometimes mercury is drawn into the plant from a mercury filled U-tube which serves for the measurement of the steam consumption. Carbon-tetrachloride should be used in pressure gages and aniline filled thermometer for the measurement of the temperatures.

D. Shut down of the plant

1. In order to prevent the deposition of salts from saturated solutions inside the pipes and apparatus during cooling periods, the solution must be recirculated and refreshed after the scrubbers have been turned off until the absorbed gases are properly purged.
2. It must be born in mind that, if the pipe which carries the live steam is cooled, the alkazid solution can be sucked back into the steam pipe through a leaking steam valve. It is advisable to provide 2 steam valves with a water drain arranged between the valves, the latter being opened as soon as the steam supply is shut off.
3. During necessary repairs the solution can be disposed of using the sump of the scrubber or the column as storage tank.

E. Methods for testing alkazid-solutions

1. Normal refreshment in the laboratory
100 cu. cm. of the solution to be tested are saturated with CO₂ and poured into a 600 cu. cm. beaker. Some pumice beads (size 3-5 mm are added). The solution is kept boiling for $\frac{1}{2}$ hour, applying a bunsen burner and an asbestos board. After cooling, the solution is decanted from the pumice beads. The beaker and the pumice beads are flushed with water which is added to the solution which is brought to the required spec. gravity of 1.200 by adding distilled water. The determination of the specific gravity is carried out at 20°C. The accuracy of the hydrometer should be previously ascertained.
If exact comparisons must be performed, the absorption values of the solution should be almost equal. The content of absorbed gases, especially that of CO₂, changes the spec. gravity of the solution, which increases with an increasing CO₂-content.

2. Absorption value (Gas-content of the solution)

It must be distinguished between:

"Blindwert" = gas content of the refreshed solution.

"Absorption value" = absorptiveness of the liquid, determined in the laboratory using pure CO₂.

"Saturation value" = Total gas content of the saturated solution

"Blindwert + absorption value.

In most cases only the "Blindwert" and absorption value are determined by trial.

The determinations of the gas-value and saturation value are carried out by treating the solution with acids and liberating the absorbed gases, whereas the absorption value is a direct determination of the absorptiveness of the solution for CO₂.

The gas value indicates how many volumes of gaseous acids (H₂S, CO₂) are present in 1 volume of the liquid.

$$\text{Gas value} = \frac{\text{Vol. gas}}{\text{Vol. liquid}}$$

The determination of the gas values (gas content) of the commercial solutions (saturated and refreshed) is the most important analysis for the supervision of the alkazid-solution. It is carried out in the following manner:

Determination of the gas valuePrinciple of the method:

A measured volume of the solution is shaken with an excess of acid. The liberated volumes of CO_2 and H_2S are measured. The apparatus which is shown in the attached picture 1 is recommended.

Procedure:

Depending on the gas value a certain volume (usually 5 cu. cm.) is poured into the annular section of flask 8, and 10 cc's of distilled water are added for dilution.

10 cu. cm. 50% H_2SO_4 are filled into the inner tube of the bottle. The bottle is closed by means of a rubber stopper, connected with an apparatus by a rubber hose, and put into a water bath at room temperature. A mixing of the acid with the alkazid solution must be carefully prevented.

After 5 minutes the bottle F has the same temperature as the water bath. The stopcocks H_1 and H_2 are opened and the level is brought to 0 in the measuring tube M by lifting the leveling bottle N where by the liquid in the tube R_2 is exactly at the same level. Stopcock H_1 is now closed and the bottle F is shaken. Gases are liberated which lower the level in M. The liberation of gases will cease after a short shaking. The bottle F is brought to room temperature by putting it in the water bath for 3 minutes. The level of the liquid in the tubes R_2 and M is brought to the same height by means of the leveling bottle N, whereafter the liberated gas volume is read in tube M. By dividing the gas volume by the volume of the solution the gas value is obtained. It is not necessary to make any corrections for the barometric pressure and the temperature.

3. Determination of the absorption value

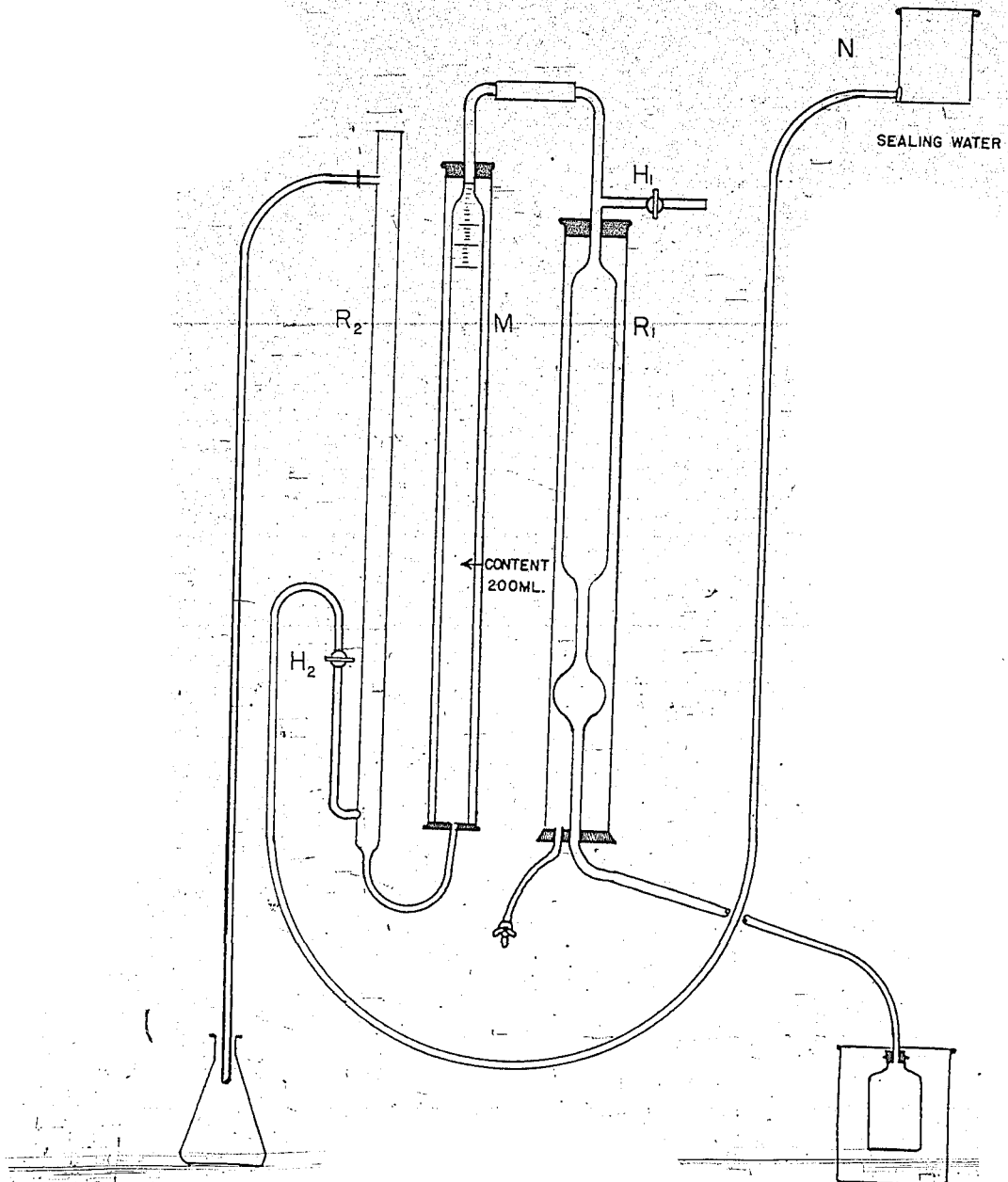
The absorption value indicates the volume of gaseous acids which can be absorbed by the alkazid solution under nearly commercial conditions. The absorption time is 2 minutes for the "M-solution" and 5 minutes for the "DK-solution". The results show the operating absorptiveness of the liquid in a scrubber used for the extraction of H_2S or CO_2 . The solution is shaken with 100% CC_2 and the absorbed volume is determined.

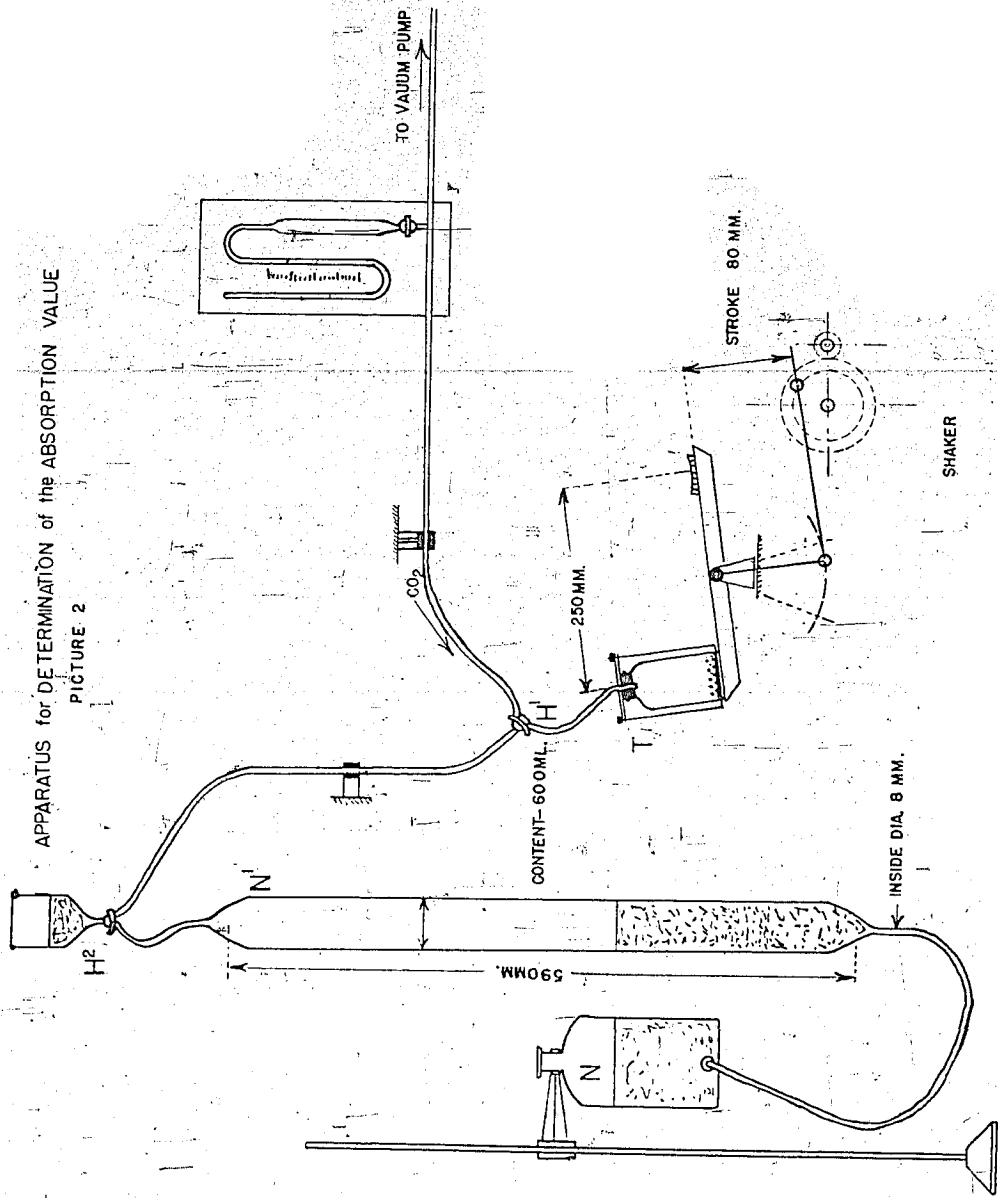
Apparatus and procedure

The apparatus is represented by picture #2. Into the 100 ccm. flask F which is made of glass or aluminum, 5 or 10 ccm. (depending on the absorptiveness) of the solution to be investigated are poured. The fresh solution (according to paragraph 1) is employed. 10 glass beads (size 5-6mm.) are added which equalize the differences of the viscosity of the various solutions, and secure a uniform mixing. The flask is now closed by means of a rubber stopper which is connected with a vacuum hose. The stopper is kept in the proper position by means of a wire clamp. The flask is mounted on a shaker, the sizes of which are represented by picture #2. The shaker is operated at 270 excursions per minute by means of an electrically driven motor. In order to evacuate the bottle F, it is connected with an air pump. With the bottle emptied it is disconnected from the air pump by means of the three way stopcock H_3 . The tube is flushed with gaseous CO_2 to the cock H_2 . The measuring vessel M is filled with 600 ccm. CC_2 where by the levels in M and N are at the same height.

The shaker is put into operation and brought to 270 excursions per minute. With the cocks H_1 and H_2 in the proper position CC_2 is introduced into the bottle. As soon as the CO_2 is absorbed by the alkazid solution, the level of the liquid rises in the vessel M. The leveling

APPARATUS FOR DETERMINATION OF GAS AND SATURATION VALUES
PICTURE I





APPARATUS for DETERMINATION of the ABSORPTION VALUE
PICTURE 2

bottle N is always kept in such a position that the level of the liquids in N and M are in the same position. After shaking for 2 or 3 minutes the tube M is closed and the absorbed volume is determined. The actual absorbed volume = total absorbed volume --- volume of the bottle (volume with the inserted stopper minus the volume of the solution and that of the glass beads). This volume divided by the volume of the employed volume of the solution is the absorption value.

4. Corrosion test

A piece of metal is used which is stamped with a number or bears another sign. The edges of the metal sheet are smoothed by means of a file. The exact weight of the piece is determined before and after the test. Since sometimes deposits on the surface of the piece are formed if long run tests are carried out, the samples are cleaned with cold water and afterwards boiled. After a final brushing, they are weighed. The corrosion is determined according to the loss of weight and the appearance of the sample.

Procedure-

100 ccm. of the alkazid solution are poured into a boiling flask which is equipped with a reflux condenser. The piece to be tested is put into the flask. The flask is put into an oil bath and kept at 130°C. for 3 days. Water vapor is condensed and led back to the flask thus maintaining a uniform specific gravity of the solution. The access of air must be carefully prevented in order to eliminate corrosion caused by oxygen. The access of air is prevented by the application of a water seal and by flushing with nitrogen.

5. Determination of the thiosulfate-sulfur of alkazid-solution

At least 5 ccm. of the solution to be tested are poured into a 500 ccm. volumetric flask which contains 100 ccm. 5% cadmium acetate solution and 10 ccm. of 1:1 acetic acid. The outlet end of the pipette must be brought underneath the surface of the liquid. The flask is vigorously shaken until the liberation of CO_2 has ceased. The solution is diluted to 500 ccm. with water. One part of the solution is filtered into a dry Erlenmeyer flask using a dry filter. 100 ccm. are titrated with $\frac{100}{N}$ or $\frac{10}{N}$ iodine solution using starch indicator.

Iodine-consumption x factor = g/liter total S as thiosulphate. The factor is 0.64 if $\frac{100}{N}$ iodine solution is employed.

" " " 6.4 if $\frac{10}{N}$ " " " " "

Such a volume of the solution must be employed so that at least 10 ccm. of the $\frac{10}{N}$ or $\frac{100}{N}$ are consumed.

6. Determination of H_2S and CO_2 in alkazid-solutions

a) H_2S

2 ccm. of the solution to be tested are poured into 5% cadmium acetate solution, immediately brought to a boil and filtered. The precipitate is washed and the filter is put into an Erlenmeyer flask which is equipped with a glass stopper and which contains 50 ccm. $\frac{10}{N}$ iodine solution which is diluted with acetic acid. After 10 minutes the excess iodine solution is titrated by $\frac{10}{N}$ sodium thio-sulphate solution.

$$1 \text{ ccm } \frac{N}{10} \text{ iodine solution} = 1.7 \text{ mg.} = 1.12 \text{ ccm } \frac{H_2S}{130/735 \text{ mm}} = 1.22 \text{ ccm. } H_2S$$

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Designating the consumed $\frac{N}{10}$ iodine solution with x and bearing in mind that 2 ccm. of the solution were employed, the factor is as follows:

$$\frac{1.12 \times X}{2} = 0.56 \times X = \text{ccm./ccm. or liter } H_2S/\text{liter alkazid-solution}$$

b) CO_2

CO_2 -content is the difference between the H_2S -content and the total gas content.